XAFS Characterization of Copper in Model Aqueous Systems of Humic Acid and Illite	X11A

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Adsorption of heavy metals at mineral surfaces and complexation with reactive organic-matter functional groups are important processes regulating the solubility and fate of soil contaminants. The objective of this study was to determine spectroscopic features that distinguish Cu(II) bonding to soil humic acid (HA) from bonding on an aluminosilicate mineral surface, and to characterize bonding in a mixed clay-organic system. EXAFS analyses were conducted on aqueous suspensions containing Cu(II) in various forms: (i) complexed with soil humic acid (HA) at various HA:Cu ratios, (ii) bound to illite, or (iii) bound in a mixture of illite and HA. Samples of pH 5.6 or 7.2 contained between 2.5 and 9 mmol Cu(II)/kg. XAFS analyses were done at Beamline X-11. Samples were analyzed in fluorescence mode at the Cu K-edge (8,979 eV) using a multielement detector. EXAFS fitting results in Table 1 show that at both pH 5.6 and 7.2, the average first-shell Cu-O bond lengths in the HA suspensions were consistently shorter than those of Cu-O in the illite suspensions (1.92 to 1.93Åversus 1.95Å, respectively). The average Cu-O bond length in the mixed illite-HA suspensions (1.94Å) was intermediate between those of the single adsorbent systems at pH 5.6, and equal to that of Cu(II) in HA at pH 7.2 (1.93Å) (Table 1). Average coordination numbers (N) and Debye-Waller factors (DW) tended to be higher in the illite suspensions compared with the HA suspensions. Although N also tended to be higher in the mixed suspensions compared with HA alone, no consistent trend in DW was observed. For the HA suspensions at pH 5.6, there appeared to be little effect of HA:Cu ratio on EXAFS results. Our results indicated that the addition of relatively low levels of HA to illite suspensions had a significant effect on average local bonding structure.

Sample	N (± 0.5)	R (Å) (± 0.01)	DW (Å^2) (± 0.0004)
Cu-acetate standard	6.0	1.95	0.0000
HA = 300 mg OC/kg, pH 5.6	5.4	1.93	0.0005
HA = 600 mg OC/kg, pH 5.6	5.8	1.93	0.0008
HA = 1200 mg OC/kg, pH 5.6	5.8	1.93	0.0009
HA = 1800 mg OC/kg, pH 5.6	5.4	1.93	0.0005
HA = 2400 mg OC/kg, pH 5.6	5.7	1.92	0.0005
illite + HA - 12.5 mg OC/kg, pH 5.6	5.9	1.94	-0.0004
illite + HA - 25 mg OC/kg, pH 5.6	6.4	1.94	0.0010
illite, pH 5.6	6.6	1.95	0.0010
HA = 300 mg OC/kg, pH 7.3	6.5	1.93	0.0011
illite + HA - 12.5 mg OC/kg, pH 7.3	6.5	1.93	0.0003
illite, pH 7.3	6.9	1.95	0.0016

Figure 1. First-shell EXAFS fitting results for Cu in humic acid (HA), illite, and mixed illite-HA suspensions using a 5 mM Cu-acetate solution as a standard (N = coordination number, R = 1st-shell bond length, and DW = Debye-Waller factor). Numbers in parentheses are parameter standard deviations given as output from the University of Washington FEFF fitting program.